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An Infrared Spectroelectrochemical Investigation of the Ion
Pairing Reactions of the Anions and Dianions of TCNE and TCNQ

by

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ABSTRACT

The infrared spectra of the dianions of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), generated electrochemically in acetonitrile, are dependent upon the supporting electrolyte. In particular, the C≡N stretching wavenumbers are higher in the presence of alkali metal salts than in the presence of tetraalkylammonium salts, and the magnitude of the shift is correlated with a positive shift in the half-wave potential of the second reduction wave. The shifts in wavenumber and half-wave potential are attributed to contact ion pairing between the dianion and the alkali metal cation. No such shifts are observed for the anion radicals of TCNE and TCNQ in acetonitrile, nor for the dianion of TCNE in dimethylsulfoxide.

AN INFRARED SPECTROELECTROCHEMICAL INVESTIGATION
OF THE ION PAIRING REACTIONS OF THE ANIONS AND DIANIONS
OF TCNE AND TCNQ

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ABSTRACT

(C-Λ triple bond)

The infrared spectra of the dianions of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ), generated electrochemically in acetonitrile, are dependent upon the supporting electrolyte. In particular, the $C \equiv N$ stretching wavenumbers are higher in the presence of alkali metal salts than in the presence of tetraalkylammonium salts, and the magnitude of the shift is correlated with a positive shift in the half-wave potential of the second reduction wave. The shifts in wavenumber and half-wave potential are attributed to contact ion pairing between the dianion and the alkali metal cation. No such shifts are observed for the anion radicals of TCNE and TCNQ in acetonitrile, nor for the dianion of TCNE in dimethylsulfoxide.

INTRODUCTION

This paper reports infrared spectra of the anion radicals and dianions of tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) in acetonitrile (AN) and dimethylsulphoxide (DMSO) solutions. The anions and dianions were generated electrochemically and the spectra were obtained by the SNIFTIRS method [1].

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TCNQ   TCNE
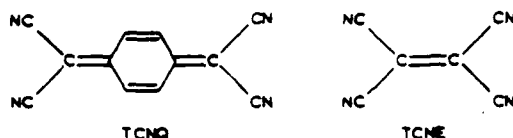
The structures of TCNQ and TCNE are shown ~~below~~ *above*. In aprotic solvents the electrochemical reduction of TCNQ and TCNE takes place in two one-electron waves, forming a stable anion radical in the first, and a stable dianion in the second.

$$R + e^- \rightleftarrows R^{\cdot-} \tag{1}$$

$$R^{\cdot-} + e^- \rightleftarrows R^{2-} \tag{2}$$

A homogeneous reproportionation reaction can also take place between the dianion and the neutral molecule to give two radical anions:

$$R^{2-} + R \rightleftarrows 2 R^{\cdot-} \tag{3}$$

In these experiments, however, this layer of solution ~~ws~~ *was* thin enough that all species within it were at equilibrium with the electrode, and since equilibrium (3) lies well to the right it could be ignored. Experiments using a thicker solution layer will be described elsewhere [2].

Cyclic voltammetric experiments in this laboratory [3] have provided evidence that strong ion pairing takes place between alkali metal cations and the dianions of TCNQ and TCNE in acetonitrile solution; the half wave potentials of the second reduction waves of TCNQ and TCNE were less negative when the supporting electrolyte was 0.1 M lithium perchlorate or sodium perchlorate than when the electrolyte was 0.1 M tetraethylammonium perchlorate (TEAP) or tetra-n-butylammonium fluoroborate (TBAF), indicating that the alkali metal cations interact with, and stabilize, the dianions. The half wave potentials of the first reduction waves were independent of supporting electrolyte, indicating that the radical anions do not form ion pairs with alkali metal cations in acetonitrile.

IR spectra can differ from one environment to another, and in particular from solid to solution. The geometry of the radical ion may be distorted in the solid state, and there is also the possibility of activation of usually infrared inactive modes through a vibronic interaction mechanism, involving distortion of the highly polarizable charge cloud of the anion by the highly polarizing counter cation to produce a dipole oscillating between anion and cation. Such a mechanism has been suggested by Devlin and co-workers to explain the appearance of a strong band at about 1370 cm^{-1} in the solid state spectra of $M^+TCNE^{\cdot-}$, where M^+ is an alkali metal cation [4–7]. It was proposed that this band is the totally symmetric C=C stretching mode of the electron cloud perpendicular to the molecular plane. Indeed *all* of the detectable infrared bands in the 600 cm^{-1} to 4000 cm^{-1} range were attributed to totally symmetric stretching modes (A_g of D_{2h}) activated by this charge oscillation mechanism. The situation is further complicated by the strong possibility that the TCNE anion radical exists as a monomer in solution at room temperature but as a

dimer in the solid state [8-10]. Some bands in the solid stated spectra of $(Na^+)_2TCNE^{2-}$ [7] and Na^+TCNQ^{-} [11] have also been attributed to vibronic activation of totally symmetric modes.

In solution the counter cation might affect the spectrum through ion pairing. For example, Eargle and Emrich [12] have found that in the fairly nonpolar solvent dimethoxyethane the C–O stretching wavenumber of the benzophenone radical anion depends upon the nature of the counteraction, the wavenumber varying from 1568 cm^{-1} in the presence of K^+ to 1575 cm^{-1} in the presence of Li^+. These shifts were attributed to ion pairing between the anions and cations.

Electrochemical generation of the radical ions allows high dielectric constant solvents and large organic counter ions to be used, Under which conditions ion pairs are less likely to form. Resonance Raman spectra of electrochemically generated $TCNE^{-}$ [13], $TCNQ^{-}$ [14] and $TCNQ^{2-}$ [15] have been obtained in acetonitrile, using TBAP as supporting electrolyte. Infrared spectra of electrochemically generated $TCNE^{-}-$ [16] and $TCNE^{2-}$ [17] have been obtained by SNIFTIRS. In the case of $TCNE^{-}$ the electrode material was platinum, and the electrolytes were TBAF and $LiClO_4$. Differences between the spectra in the two electrolytes were attributed to absorption of the anion only in the presence of TBAF. In the case of $TCNE^{2-}$ the electrode material was carbon, the electrolyte was TBAF, and the spectrum was attributed to $TCNE^{2-}$ adsorbed and in solution.

The spectra described here were obtained with $LiClO_4$, $NaClO_4$, TEAP, and TBAF as electrolytes, in order to study the effects of ion pairing.

EXPERIMENTAL

For most experiments the spectrometer was a Digilab Qualimatic instrument with a cooled (77K) HgCdTe detector. The spectrometer was purged with nitrogen and the cell was situated outside it. The cell and other instrumentation have been described in detail elsewhere [1]. The working electrode was a 7 mm diameter platinum, gold, or vitreous carbon disk mounted on the end of a brass shaft inside a 9 mm diameter Kel-F tube. The electrode was pushed up against a CaF_2 infrared-transparent window, forming a thin-layer cell. Thin layer voltammetry showed the average window to electrode distance to be 50 μm. The window had a trapezoidal cross-section, allowing equal transmission of s- and p-polarized light. For acetonitrile solutions the reference electrode was a silver wire in contact with $AgNO_3$ (0.01 M) and TBAF (0.1 M) in acetonitrile. For DMSO solutions an SCE was used. All electrode potentials in acetonitrile are referred to the Ag/Ag^+ (0.01 M) electrode, and in DMSO to the SCE.

Sodium perchlorate (GFS) was recrystallized twice from triply distilled water. Anhydrous lithium perchlorate (GFS) was used as received. TBAF was prepared according to the method of Lund and Iverson [18] and recrystallized from methylene chloride and distilled water. TEAP (Eastman, reagent grade) was recrystallized twice from triply distilled water. Reagent grade TCNE (Eastman) was recrystallized twice from chlorobenzene. Reagent grade TCNQ (Eastman) was used as received. Acetonitrile (Burdick and Jackson UV grade, water content nominally 0.009%) and

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DMSO (Burdick and Jackson, water content nominally 0.015%) were dried over Woelm neutral alumina (Supergrade I) before use.

For each system interferograms were collected at three potentials: one where the neutral species was stable, one where only the anion radical could coexist with the electrode, and one where only the dianion could coexist with the electrode. Usually 128 interferograms at 4 cm^{-1} resolutions were collected at each potential. Ratioing two of the three averaged interferograms gave, after Fourier transformation, difference spectra where bands pointing down arise from species present only at the more negative potential, and bands pointing up are due to species present only at the more positive potential.

RESULTS

The anions of TCNE

Figures 1, 3, and 5 show SNIFTIRS spectra of the TCNE (5 mM)/TBAF (0.1 M)/AN and TCNE (5 mM)/LiClO$_4$ (0.1 M)/AN systems in the C≡N stretching
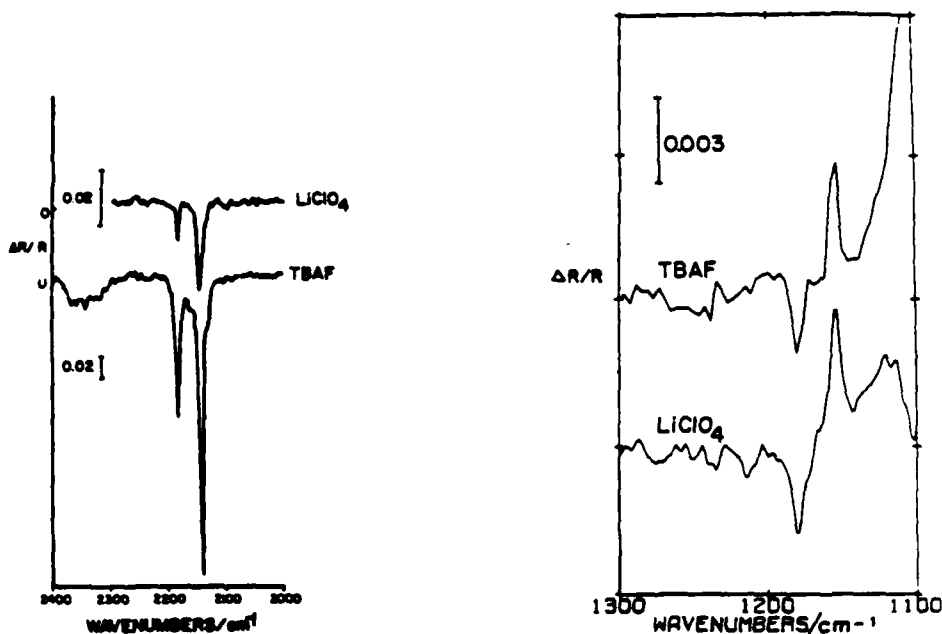

Fig. 1. SNIFTIRS difference spectrum in C≡N stretching region for reduction of TCNE to TCNE$^{.-}$ at a platinum electrode. Solution thickness ca 50 μm. Solutions contained TCNE (5 mM) in acetonitrile with 0.1 M LiClO$_4$ (top spectrum) and 0.1 M TBAF (bottom spectrum) as supporting electrolyte. Potential modulated from +0.5 V to −0.5 V (vs. Ag/0.01 M Ag$^+$ reference).

Fig. 2. SNIFTIRS spectrum in C-C stretching region for reduction of TCNE to TCNE$^{.-}$ at a platinum electrode. Same parameters as Fig. 1.
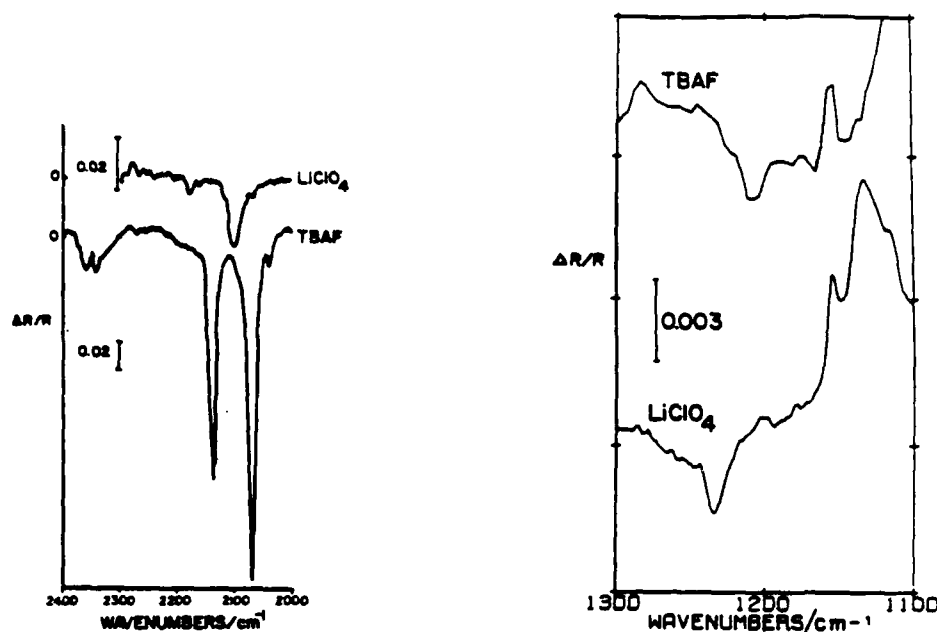
Fig. 3. SNIFTIRS difference spectrum in C≡N stretching region for reduction of TCNE to $TCNE^{2-}$ at a platinum electrode. Solution thickness ca 50 μm. Same solutions as Fig. 1. Top spectrum: 0.1 M $LiClO_4$ as supporting electrolyte, potential modulated from +0.5 V to -1.2 V. Bottom spectrum: 0.1 M TBAF as supporting electrolyte, potential modulated from -0.5 V to -2.0 V.

Fig. 4. SNIFTIRS difference spectrum in C-C stretching region for reduction of TCNE to $TCNE^{2-}$ at a platinum electrode. Same parameters as Fig. 3.

region. The only other detectable bands are in the 1100-1300 cm^{-1} region, and these are shown in Figs. 2, 4, and 6. (Noise spikes at 1160 and 1230 cm^{-1} have been subtracted out of the TBAF spectra in Figs. 4 and 6.) A platinum electrode was used to generate the anions for these spectra, but similar spectra were obtained using pyrolytic graphite and gold electrodes. All bands could be observed with either s-polarized or p-polarized radiation, so all must arise from species which are in solution rather than on the electrode surface. Bands obtained in the presence of $LiClO_4$ were usually weaker than bands obtained in the presence of TBAF, apparently because some precipitation of Li_2TCNE salt often takes place when $TCNE^{2-}$ is generated in the presence of Li^+. When TEAP was used as electrolyte the spectra were identical to those obtained with TBAF as electrolyte.

Figures 1 and 2 show SNIFTIRS spectra taken at -0.4 V (vs. Ag/Ag^+), where $TCNE^{·-}$ is stable, with reference potential +0.4 V, where TCNE is stable. The C≡N stretching bands of TCNE are apparently too weak to be seen, but there are negative going bands from $TCNE^{·-}$ at 2187 and 2146 cm^{-1}. At lower wavenumbers
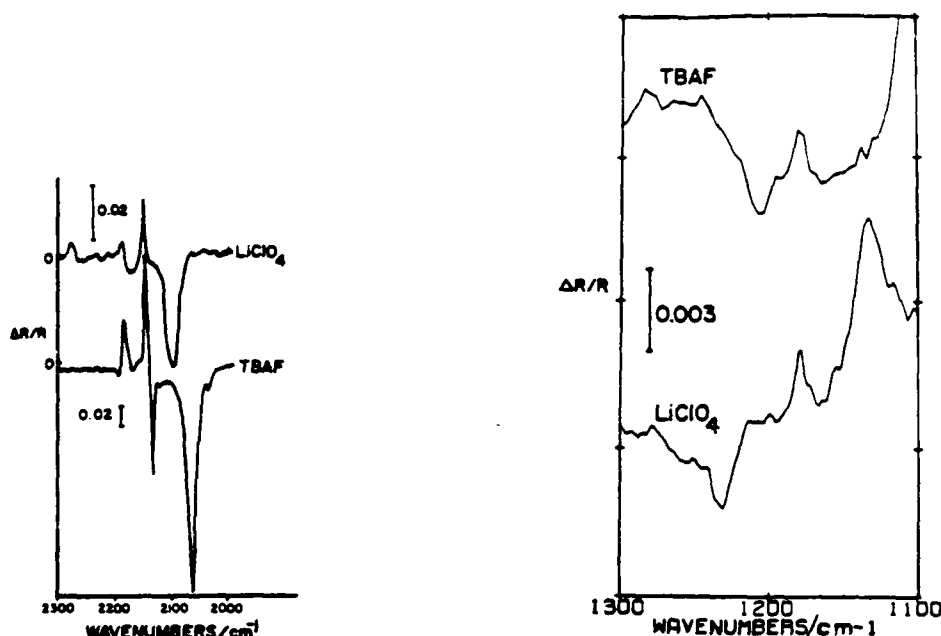
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Fig. 5. SNIFTIRS difference spectrum in C≡N stretching region for reduction of TCNE·⁻ to TCNE²⁻ at a platinum electrode. Solution thickness ca 50 μm. Same solutions as Fig. 1. Top spectrum: 0.1 M LiClO₄ as supporting electrolyte, potential modulated from −0.5 V to −1.2 V. Bottom spectrum: 0.1 M TBAF as supporting electrolyte, potential modulated from −0.5 V to −2.0 V.

Fig. 5. SNIFTIRS difference spectrum in C–C stretching region for reduction of TCNE·⁻ to TCNE²⁻ at a platinum electrode. Same parameters as Fig. 5.

there is a positive going band from TCNE at 1155 cm⁻¹, and a negative going band from TCNE·⁻ at 1180 cm⁻¹. The wavenumbers of all of these bands are independent of electrolyte.

Figures 3 and 4 show SNIFTIRS spectra for electrogeneration of TCNE²⁻ in the presence of TBAF and LiClO₄. The reference potential was again +0.4 V. While the spectrum of TCNE·⁻ in acetonitrile is independent of electrolyte, this is clearly not the case for TCNE²⁻. With TBAF as electrolyte the dianion has two C≡N stretch bands at 2141 and 2075 cm⁻¹, and a band at 1207 cm⁻¹.

Spectra taken with reference potential −0.4 V where the anion radical is stable and with working potentials where the dianion is stable are shown in Figs. 5 and 6. As expected, positive going bands from TCNE·⁻ are observed at 2187, 2146 and 1180 cm⁻¹ with both electrolytes, and negative going bands from TCNE²⁻ are observed at 2141, 2075, and 1207 cm⁻¹ with TBAF electrolyte and at 2175, 2102, and 1232 cm⁻¹ with LiClO₄.

The anions of TCNQ

SNIFTIRS spectra in the C≡N stretching region for the TCNQ (5 mM)/TBAF (0.1 M)/AN and TCNQ (5 mM)/LiClO$_4$ (0.1 M)/AN systems are shown in Figs. 7 and 8. TEAP and NaClO$_4$ were also used as electrolytes; TEAP again gave the same spectra as TBAF. A platinum electrode was used for all of these experiments. All bands reported here are due to solution species, because all could be observed with either s- or p-polarized radiation.

The spectrum of TCNQ$^{.-}$ (Fig. 7), taken with working potential at -0.2 V and reference potential $+0.4$ V, shows two C≡N str bands for TCNQ$^{.-}$, at 2182 and 2156 cm^{-1}, and a weaker band for TCNQ at 2224 cm^{-1} (see Table 1).

Fig. 7. SNIFTIRS difference spectrum in C≡N stretching region for reduction of TCNQ to TCNQ$^{.-}$ at a platinum electrode. Solution thickness ca 50 μm. Solutions contained TCNQ (5 mM) in acetonitrile with 0.1 M LiClO$_4$ (top spectrum) and 0.1 M TBAF (bottom spectrum) as supporting electrolyte. Potential modulated from $+0.4$ V to -0.2 V (vs. Ag/0.01 M Ag$^+$ reference).
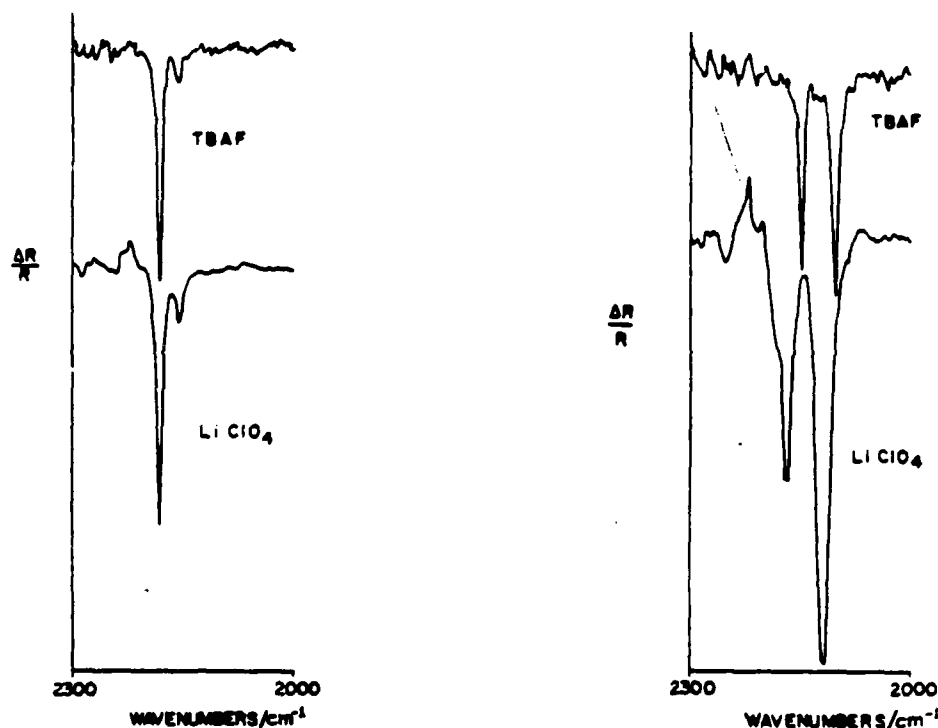
Fig. 8. SNIFTIRS difference spectrum in C≡N stretching region for reduction of TCNQ to TCNQ^{2-} at a platinum electrode. Solution thickness ca 50 μm. Same solutions as Fig. 7. Top spectrum: 0.1 M LiClO$_4$ as supporting electrolyte, potential modulated from $+0.4$ V to -0.2 V. Bottom spectrum: 0.1 M TBAF as supporting electrolyte, potential modulated from -0.4 V to -1.2 V.

TABLE 1

Infrared vibrational wavenumbers of TCNE and its anions in acetonitrile

Mode	Vibrational wavenumber/cm^{-1}				
	TCNE [a]	TCNE [b]	TCNE·$^{-}$ [b,c]	TCNE^{2-}/TBA^{+} [b,d]	TCNE^{2-}/Li^{+} [b]
$\nu_{15}(B_{2u})$	2263		2185	2141	2175
$\nu_{9}(B_{1u})$	2230		2145	2070	2102
$\nu_{2}(A_{g})$					1232
$\nu_{16}(B_{2u})$	1155	1155	1180	1207	
$\nu_{10}(B_{1u})$	958				

[a] Ref. 10.
[b] This work.
[c] Same wavenumbers for TCNE·$^{-}$/TBA^{+}, TCNE·$^{-}$/TEA^{+}, and TCNE·$^{-}$/Li^{+} systems.
[d] Same wavenumbers for TCNE^{2-}/TBA^{+} and TCNE^{2-}/TEA^{+} systems.

The C≡N str bands of TCNQ^{-} (Fig. 8) show similar behavior to those of TCNE^{2-}; the wavenumbers are lower than those of TCNQ·$^{-}$ and depend upon the electrolyte. With TBAF and TEAP these bands are at 2153 and 2106 cm^{-1}, with NaClO$_4$ they are at 2156 and 2110 cm^{-1}, and with LiClO$_4$ they are at 2166 and 2118 cm^{-1}. (The positions of other bands are listed in Table 2.)

Experiments where the concentration of LiClO$_4$ was varied between 0.001 M and 0.1 M (while that of TBAF was half constant at 0.1 M) produced no new bands, suggesting that a complex of only one stoichiometry, probably 1 : 1, is formed.

The same experiments were carried out in DMSO with TBAF and LiClO$_4$ as electrolytes. In this solvent no evidence for ion pairing was obtained; the half wave potentials of both reduction waves of TCNQ were independent of electrolyte, and the C≡N str wavenumbers of the anions TCNQ·$^{-}$ and TCNQ^{2-} did not depend on

TABLE 2

Infrared vibrational wavenumbers of TCNQ and its anions in acetonitrile

Mode	Vibrational wavenumbers/cm^{-1}				
	TCNQ	TCNQ·$^{-}$ [a]	TCNQ^{2-}/TBA^{+} [b]	TCNQ^{2-}/Na^{+}	TCNA^{2-}/Li^{+}
$\nu_{19-u})$	2224	2182	2153	2156	2166
$\nu_{33}(B_{2u})$	2224	2156	2106	2110	2118
			1576		
	1545	1506	1501		1501
			1493		1493
		1362	1296		1296
		1209	1225		1235
		986			
	845	833	821		821

[a] Same wavenumbers for TCNQ·$^{-}$/TBA^{+}, TCNQ·$^{-}$/TEA^{+}, TCNQ·$^{-}$/Na^{+} and TCNQ·$^{-}$/Li^{+} systems.
[b] Same wavenumbers for TCNQ^{2-}/TB·$^{+}$ and TCNQ^{2-}/TEA^{+} systems.

electrolyte either. In fact these wavenumbers (2180 and 2153 cm^{-1} for the anion, 2151 and 2104 cm^{-1} for the dianion) are the same as those of uncomplexed TCNQ^{-} and TCNQ^{2-} in acetonitrile.

DISCUSSION

TCNE is planar and belongs to the D_{2h} point group. It has four C≡N groups and therefore four C≡N stretching modes. Two of these, the $\nu_9(B_{1u})$ and $\nu_{15}(B_{2u})$ modes, are infrared active and Raman inactive, while the other two, the $\nu_1(A_g)$ and $\nu_{19}(B_{3g})$ modes, are Raman active and infrared inactive. Similarly there are four modes of mostly C–C stretching character: IR active $\nu_{10}(B_{1u})$ and $\nu_{16}(B_{2u})$ modes, and Raman active $\nu_3(A_g)$ and $\nu_{21}(B_{39})$ modes. The only other in-plane stretching mode is the Raman active $\nu_2(A_g)$ mode, which is mostly stretching of the central C≡C bond. The transmission IR spectrum [6] of neutral TCNE has bands at 2263, 2230, 1155, and 958 cm^{-1}, and these have been assigned to the ν_{15}, ν_9, ν_{16}, and ν_{10} modes respectively. (Actually, for neither neutral TCNE nor for its anions is it really known which C≡N stretch band corresponds to ν_{15} and which to η_9.) TCNE also has bands at lower wavenumbers which have been assigned to bending vibrations. If TCNE^{-} and TCNE^{2-} are planar and undistorted (i.e., of D_{2h} symmetry), they should also have two IR active C≡N stretch modes (ν_{15} and ν_9) and two IR active C–C stretch modes (ν_{16} and ν_{10}).

While there have been other assignments of the TCNE^{-} bands [16], it appears simplest to assign them to the normally infrared active modes of a species with D_{2h} symmetry. Then the 2187 and 2146 cm^{-1} bands correspond to the ν_{15} and ν_9 C≡N stretching modes, and the 1155 and 1180 cm^{-1} bands to the ν_{16} C–C stretching mode. These assignments are summarized in Table 1. The ν_{10} C–C stretch could not be observed because it is below the 1000 cm^{-1} cutoff of the CaF$_2$ window used here. The spectra therefore show that addition of an electron to TCNE weakens the C≡N bonds and strengthens the C–C bonds. This is consistent with MO calculations [19–25] which show that both additional electrons go into an orbital which is antibonding w.r.t. the C≡N bonds, bonding w.r.t. and C–C bonds, and antibonding w.r.t. the central C≡C bond. The spectrum of TCNE^{-} in solution (Table 1) is quite different from the spectrum of TCNE^{-} in solid NaTCNE [7] state. In particular, the C≡N str wavenumbers are higher in the solid state spectrum (2222 and 2188 cm^{-1}), and the solid-state spectrum has additional bands at ca. 1400 cm^{-1}. The appearance of the bands around 1400 cm^{-1} has been attributed to infrared activation of the A_g C=C stretching mode by an interaction of the anion and cation [4–7]. This interaction could also increase the C≡N str wavenumbers in the same manner as does the interaction of Li$^+$ with the dianion (cf. Fig. 3). The situation is complicated, however, by the probability of bonding between adjacent TCNE^{-} units in te solid state [8–10], which may also cause changes in bond orders and in selection rules.

Again, it is simplest to assign the observed bands for TCNE^{2-} to the ν_{15}, ν_9, and ν_{16} modes, assuming that TCNE^{2-} has D_{2h} symmetry (see Table 1). This would

mean that, as predicted by the MO calculations, addition of an electron to $TCNE^{\cdot-}$ causes further weakening of the $C\equiv N$ bonds and further strengthening of the C–C bonds. With $LiClO_4$ as electrolyte, the dianion bands are at 2175, 2102, and 1232 cm^{-1}. The $C\equiv N$ bands are shifted to lower wavenumber compared to the anion radical, but not by as large an amount as in the presence of TBAF. This difference is attributed to strong ion pairing of $TCNE^{2-}$ with Li^+ and not with $(C_4H_9)_4N^+$. Presumably the Li^+ ion either undergoes a charge-transfer interaction with $TCNE^{2-}$ which removes some electron density from the antibonding MO, or it causes a redistribution of π-electrons within the dianion such that the $C\equiv N$ bonds are strengthened. It seems likely that only one Li^+ ion is involved in this strong interaction with $TCNE^{2-}$, because experiments using mixtures of TBAF (0.1 M) and $LiClO_4$ (0.001 M to 0.1 M) showed only the two sets of $C\equiv N$ stretch bands of Fig. 3. No additional bands appeared at low Li^+ concentrations, as might be expected if there were complexes of more than one stoichiometry. (This does not rule out weak interactions of other Li^+ ions with the complex.) The 1232 cm^{-1} band of the complex presents a problem. It is at higher wavenumbers than the ν_{16} C–C stretch of uncomplexed $TCNE^{2-}$, yet it is difficult to conceive of a mechanism which could simultaneously strengthen both the $C\equiv N$ and C–C bonds of example $TCNE^{2-}$. It is more likely that the 1232 cm^{-1} band is the normally infrared inactive $\nu_2(A_g)$ C=C stretching vibration. This mode could be made infrared active by distortion of the π-electron cloud of the dianion in the direction of the cation, which is probably sitting above the molecular plane, causing vibration of the C=C bond to give rise to an oscillating dipole normal to the molecular plane. It has been proposed, in fact, that this mechanism of activation of the ν_2 mode is responsible for bands in the solid state infrared spectra of $M^+TCNE^{\cdot-}$ and $(Na^+)_2TCNE^{2-}$ at ca. 1400 cm^{-1} [4–6] and 1260 cm^{-1} [7] respectively. Possible structures of the $TCNE^{2-}Li^+$ complex will be considered in more detail below.

The $C\equiv N$ stretching wavenumbers of solid Na_2TCNE are, quite reasonably, intermediate between those of uncomplexed $TCNE^{2-}$ and the $TCNE^{2-}-Li^+$ ion pair. The dianion appears to have an IR active C=C stretching mode and an IR inactive C–C stretching mode both in the ion pair and in the solid state, which suggests that the two environments are quite similar.

TCNQ is similar to TCNE in that it is planar and of D_{2h} symmetry. Therefore TCNQ and its anions, if they are also planar, each have two infrared active $C\equiv N$ stretch modes, which are labeled $\nu_{19}(B_{1u})$ and $\nu_{33}(B_{2u})$. For neutral TCNQ these two modes are coincident at 2228 cm^{-1} [11].

There are a number of bands at lower wavenumbers than the CN str bands, and these are listed in Table 2. Because of the complexity of the molecule, and because of uncertainty in the literature [11,26], no attempt is made here to assign these other bands. The positions of all bands of $TCNQ^{\cdot-}$ are independent of electrolyte. The lowest unoccupied molecular orbital of TCNQ, into which the additional electrons must go, is antibonding with respect to the $C\equiv N$ bonds, just as it is for TCNE. In accordance with this, the $C\equiv N$ str wavenumber of $TCNQ^{\cdot-}$ are lower than that of TCNQ.

TABLE 3

Electrochemical and infrared data for the reductions of TCNE and TCNE·⁻ in acetonitrile

Reaction electrolyte cation	TCNE + e^- → TCNE·			TCNE·⁻ → TCNE²⁻		
	TBA⁺	Na⁺	Li⁺	TBA⁺	Na⁺	Li⁺
$E_{1/2}$/V (vs. Ag/Ag⁺)	−0.07	−0.07	−0.07	−1.05	−0.94	−0.79
ν_{CN} decrease/cm⁻¹	82		82	59		26
ν_{CN} splitting/cm⁻¹	40		40	71		73

The anticipated weakening of the C≡N bonds occurs upon adding the second electron, but the wavenumber shifts are smaller in the presence of alkali metal cations, and once again this is attributed to complex formation with the small cations.

The SNIFTIRS spectrum of TCNQ·⁻ (Table 2) agrees very well with the IR spectrum of LiTCNQ in acetonitrile [26]. The solid state IR spectra of alkali metal salts of TCNQ·⁻ [11,26] show C≡N stretching wavenumbers which are higher than those of solution free TCNQ·⁻, and which increase with decreasing size of the cation, presumably because of interactions between the cations and the anion.

There are close similarities between the solution spectra of TCNQ²⁻ (Table 2) and the solid state spectrum of Na₂TCNQ [11], which has strong bands at 2164, 2096, 1503, 1498, 1303, 1238, and 822 cm⁻¹, and weaker bands at 1598, 1435, and 1353 cm⁻¹. The average C≡N str wavenumber of Na₂TCNE (2130 cm⁻¹) is close to that of the TCNQ²⁻–Na⁺ ion pair (2133 cm⁻¹), but the splitting is greater in the solid state.

Cyclic voltammetry provided the first evidence for ion pairing between alkali metal cations and the dianions of TCNE and TCNQ in acetonitrile; the half wave potentials ($E_{1/2}$) of the second reduction waves varied with electrolyte, while the half wave potentials of the first reduction waves did not [3]. Further evidence for ion pairing comes from the electrolyte dependence of the C≡N stretching wavenumbers of TCNE²⁻ and TCNQ²⁻. Tables 3–5 compare the half wave potential of each reduction wave in the TCNE/AN, TCNQ/AN, and TCNQ/DMSO systems with the difference in average C≡N str wavenumber between the oxidized and reduced species. Also shown is the splitting between the two C≡N str bands of the reduced species. A number of points are apparent from these Tables:

TABLE 4

Electrochemical and infrared data for the reductions of TCNQ and TCNQ·⁻ in acetonitrile

Reaction electrolyte cation	TCNQ + e^- → TCNQ·⁻			TCNQ·⁻ + e^- → TCNQ²⁻		
	TBA⁺	Na⁺	Li⁺	TBA⁺	Na⁺	Li⁺
$E_{1/2}$/V (vs. Ag/Ag⁺)	−0.11	−0.11	−0.11	−0.66	−0.63	−0.52
ν_{CN} decrease/cm⁻¹	55	55	55	39	36	27
ν_{CN} splitting/cm⁻¹	26	26	26	47	47	48

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TABLE 5

Electrochemical and infrared data for the reductions of TCNQ and TCNQ$^{\cdot-}$ in DMSO

Reaction electrolyte cation	TCNQ + e^- → TCNQ$^{\cdot-}$		TCNQ$^{\cdot-}$ + e^- → TCNQ^{2-}	
	TBA$^+$	Li$^+$	TBA$^+$	Li$^+$
$E_{1/2}$/V vs. SCD	+0.29	+0.29	−0.26	−0.26
ν_{CN} decrease/cm^{-1}	54	54	39	39
ν_{CN} splitting/cm^{-1}	27	27	47	47

(i) For neither anion radical is there any evidence of ion pairing with alkali metal cations.

(ii) The half wave potentials for reduction of the anion radicals to the dianions [3] in acetonitrile become less negative when TBAF or TEAP electrolytes are replaced with lithium or sodium perchlorate. This shows that the dianions are stabilized by interaction with the small alkali metal cations.

(iii) Li$^+$ causes a greater positive shift in $E_{1/2}$ than does Na$^+$ [3]. It was determined that the ion pairs are of the contact rather than the solvent separated type.

(iv) When the half wave potentials indicate that ion pairs are formed, shifts in the C≡N str wavenumbers are also observed. In fact, ion pairing causes a shift to higher wavenumber which is roughly proportional to the positive shift in $E_{1/2}$. To see why this is so, we point out pertinent information regarding the structures of the ion pairs. It is most likely that only one cation interacts strongly with each dianion, because decreasing the the concentration of metal ion fails to reveal any new bands. This cation would probably be situated in the center of the π-electron cloud above the molecular plane of the dianion; a less symmetrical location would give rise to four IR active C≡N stretch modes, instead of the two which are observed. (This location would also nicely account for the infrared activation of the central C=C bond in the TCNE^{2-}-Li$^+$ complex.) According to a simple electrostatic model, placing a cation over the central C=C bond of TCNE^{2-} would increase the contribution of resonance structures such as
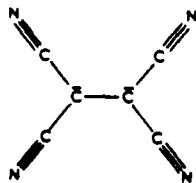
relative to structures such as
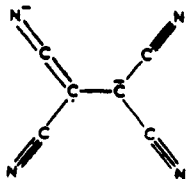
Similar considerations apply to $TCNQ^{2-}$; placement of a cation over the center of the six-membered ring would increase contributions from resonance structures where the $C\equiv N$ triple bond is intact. This accounts qualitatively for the increase in $C\equiv N$ str wavenumber caused by ion pairing. (Note that if the cation was associated with an N atom, a decrease in $C\equiv N$ str wavenumber would be expected.) According to this model, then, the shift in $E_{1/2}$ and shift in $C\equiv N$ str wavenumber are related; neglecting changes in solvation of the dianion and cation, the shift in $E_{1/2}$ measures the energy of electrostatic interaction of the cation with the negative charges on the dianion, and the shift in $\bar{\nu}_{CN}$ measures the ability of the cation to pull negative charge off the nitrogen atoms and towards the center of the molecule. Therefore both the shift in $E_{1/2}$ and the shift in $\bar{\nu}_{CN}$ increase with decreasing size of the cation and decreasing size of the dianion.

(v) While the average position of the $C\equiv N$ str bands of the dianions are affected by ion pairing, their splitting is predicted to be independent of ion pairing interactions. In fact it appears that the difference in the two $C\equiv N$ stretch bands for the dianions is directly proportional to the charge per π-bonded atom in the molecule, the constant of proportionality being 390 cm^{-1}.

(vi) There is no strong ion pairing between $TCNQ^{2-}$ and Li^{+} in DMSO. Presumably the loss of solvation of Li^{+} upon ion pair formation makes this process unfavorable in DMSO. (The solvation energy of Li^{+} is higher in DMSO than in acetonitrile, the Gutman donor numbers in these two solvents being 30 and 14, respectively [27].)

CONCLUSIONS

(i) Strong contact ion pairing takes place in acetonitrile between alkali metal cations and the dianions of TCNE and TCNQ. The spectra of the ion pairs are quite similar to the solid state spectra of the dianions.

(ii) Ion pairing shifts the $C\equiv N$ stretch bands of $TCNE^{2-}$ and $TCNQ^{2-}$ to higher wavenumber without changing the number of these bands nor the splitting between them. This is consistent with location of a cation above the central $C=C$ bond in $TCNE^{2-}$ and above the six-membered ring in $TCNQ^{2-}$.

(iii) Ion pairing appears to make infrared active the (totally symmetric) $C=C$ stretching vibration of $TCNE^{2-}$.

(iv) The spectrum of $TCNE^{2-}$ in acetonitrile is the same in the presence of TEAP as it is in the presence of TBAF. This means that the large difference in the standard heterogeneous rate constant of the $TCNE^{-}TCNE^{2-}$ couple in these two systems [3] cannot be due to differences in the structure of the dianion, and must instead be due to surface effects such as distance dependent electron transfer rates or different potential distributions in the double layer.

(v) There is no strong ion pairing in acetonitrile or DMSO between alkali metal cations and the anion radicals of TCNE and TCNQ. The spectra are very different from the solid state spectra of $TCNE^{-}$ and $TCNQ^{-}$ for that reason.

(vi) There is no strong ion pairing in DMSO between Li^{+} and $TCNQ^{2-}$, probably because of strong solvation of Li^{+} by DMSO.

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